

Dynamic Nuclear Polarization NMR Spectroscopy Allows High Throughput Characterization of Microporous Organic Polymers

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Supporting Information Placeholder

ABSTRACT: Dynamic nuclear polarization (DNP) solid-state NMR was used to obtain natural abundance ¹³C and ¹⁵N CP MAS NMR spectra of microporous organic polymers with excellent signal to noise ratio, allowing for unprecedented details in the molecular structure to be determined for these complex polymer networks. Sensitivity enhancements larger than 10 were obtained with bis-nitroxide radical at 14.1 T and at low temperature (~105 K). This DNP MAS NMR approach allows efficient, high throughput characterization of libraries of porous polymers prepared by combinatorial chemistry methods.

Microporous organic polymers (MOP) have found an increasing number of applications recently in heterogeneous catalysis, adsorption, separation, and in energy production and storage.¹ For all of these applications, which typically involve the incorporation of functional monomers, it is important to understand the solid state structure and composition of the MOPs. Unlike crystalline porous frameworks, MOPs are generally amorphous, and hence structures cannot be determined by X-ray crystallography. Also, porous networks are insoluble, precluding solution-phase characterization methods.

Solid-state nuclear magnetic resonance (NMR) spectroscopy experiments are among the most powerful tools available for structure elucidation of molecules and materials. NMR has always been central to polymer chemistry,² allowing the local conformation of macromolecules to be determined. Recently, our group³ and others⁴ have used solid-state NMR spectroscopy extensively to confirm that the solid state structures of microporous polymers are consistent with the

monomer feed,^{3,5} albeit with experimental times often exceeding many hours or days. This renders the approach incompatible with the preparation of libraries of materials using modern high throughput techniques, for example to generate conjugated microporous polymers (CMPs) with a wide range of chemical functionalities.^{1c}

High field dynamic nuclear polarization (DNP)⁶ offers dramatic enhancements in the sensitivity of magic angle spinning (MAS) solid-state NMR experiments using a transfer of polarization from electron spins, in mono⁷ or biradicals,⁸ to nuclear spins. DNP is being exploited to tackle structural challenges associated with a wide range of biomolecules⁹ and materials.¹⁰ Polymers such as polystyrene and polycarbonate doped with BDPA free-radical complex with benzene¹¹ or bisphenol A polycarbonate doped with trianisylaminiumperchlorate, trianisylamine¹² or BDPA^{11a,13} as the source of electrons were also investigated, mostly focusing on polymer blend interfaces. MAS DNP enhancement was observed in poly(methyl methacrylate) sub-micron particles using a pulse microwave DNP spectrometer,¹⁴ and very recently, on functionalized synthetic polymer (such as polystyrene and poly(ethylene oxide)) with a setup similar to the one used here.¹⁵

We demonstrate here that the gain of sensitivity associated with DNP-enhanced solid-state NMR spectroscopy at 14.1 T can be used for the high throughput molecular structure determination of dozens of MOP materials in a rapid fashion (Fig. 1). We first validated that state-of-the-art incipient wetness sample impregnation using a solution of biradical bCTbK^{8c,d} in 1,1,2,2-tetrachloroethane solvent¹⁶ yields good signal enhancement for ¹H ¹³C cross polarization (CP) MAS NMR experiments (Fig. 2) on **P1**^{3a} networks and on a new

MOP network containing 15 % of 4-aminobenzene functionality **P1-NH₂-15** (see the Supporting Information (SI) for details of all sample preparations). We then showed that this can be used to confirm the structures of a large range of MOPs **P1-R-X** (having various end-groups, **R**, and end-group concentrations, **X**) with the hypothetical networks shown in Fig. 1. This was done by identification of a carbon or nitrogen fingerprint signal of the MOP in the ¹H ¹³C or ¹H ¹⁵N CP MAS DNP spectra (Fig. 3-4).

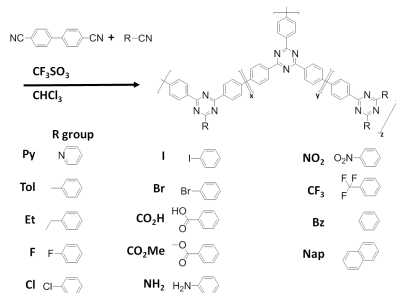


Figure 1. Synthesis of triazine-based MOP **P1-R-X**. 4,4'-biphenyldicarbonitrile and a mononitrile aromatic functionality (R-groups) were trimerized to yield an insoluble polymer. Mononitrile functionalities were incorporated at 15 % or 30 % molar in the feed. The polymer may include three different repeat units: triazine rings with one adjacent R-group (x), triazine rings connected to three other triazines (y) or triazine rings connected to two R-groups (z).

Figure 2a shows the ¹H ¹³C CP MAS DNP spectra of MOP network **P1** obtained with and without microwave (MW) irradiation. An observed DNP enhancement value of $\epsilon_{\text{C CP}} = 13$ was obtained (determined as the signal intensities ratio with and without microwave, and measured on the biphenyl carbons at 129 ppm), thus allowing one-dimensional ¹³C spectrum with good signal to noise ratio to be acquired very quickly (10 min). To obtain the same signal to noise ratio ¹³C spectrum without DNP, it was shown experimentally that the spectrum requires about 6 h of acquisition time (see SI). The enhancement of the solvent ¹³C signal was found to be similar ($\epsilon_{\text{S}} = 14$), in agreement with the bCTbK radical (approximate size $\sim 1.5 \times 1 \text{ nm}$)^{8c} being located *inside* the pore of **P1**¹⁷ (as also found for other frameworks).¹⁸ Although most of the porosity in **P1** arises from pores smaller than $\sim 1.6 \text{ nm}$, according to the pore size distribution of the dry materials (see SI), it should be remembered that these materials could also swell in solvent.^{1c,19} Higher DNP enhancement values on model samples have been reported although they were obtained on different DNP spectrometer design,^{6c,20} at lower temperatures, fields and MAS frequencies.^{6c,8b,20b,21} Attempts to increase the DNP enhancement $\epsilon_{\text{C CP}}$ at 14.1 T using other conditions yield values of only 4-9 (see SI) possibly due to the lack of homogeneous glass formation, high proton density and/or poor crystallinity,^{10f} although similar values were obtained at 14.1 T previously.^{20a}

Solid-state NMR is the only technique available to characterize the structure of these amorphous polymer networks at

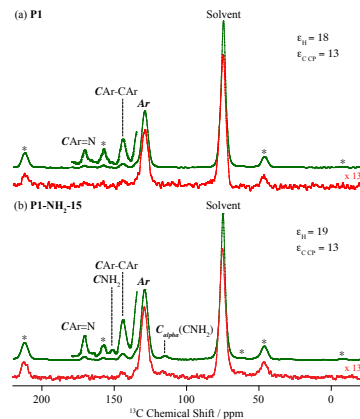


Figure 2. ¹H ¹³C CP MAS spectrum of (a) **P1**^{3a} and (b) **P1-NH₂-15** recorded with (green) and without (red) microwave irradiation at $\nu_0(\text{e}^-) = 395.2 \text{ GHz}$. All the spectra were recorded on a Bruker 14.1 T DNP Avance III solid-state NMR spectrometer^{6c} at sample temperature of $\approx 105 \text{ K}$ with $\nu_0(^1\text{H}) = 600.084 \text{ MHz}$ and $\nu_0(^{13}\text{C}) = 150.905 \text{ MHz}$ under $\nu_{\text{rot}} = 12.5 \text{ kHz}$ and SPINAL-64 ¹H decoupling²² with $\nu_1(^1\text{H}) = 100 \text{ kHz}$. 64 (in (a)) and 256 (in (b)) scans with a 10 s recycle delay and a 2 ms CP contact time were averaged (experimental time = 10 min in (a) and 43 min in (b)). Samples were wet with 10 mM bCTbK^{8c} in C₂Cl₄H₂ solution.¹⁶ ϵ_{H} and $\epsilon_{\text{C CP}}$ signal enhancement factors are given in the figure. Spinning sidebands are marked with asterisks. Inserts show a magnified view (x 6) of the 180-135 ppm region.

a molecular level, and DNP efficiency allows more detail to be determined than would usually be possible in a realistic timeframe. The various resonances in the ¹³C spectra for **P1** (Fig. 2) could be assigned as follows: the peaks at 129 and at 135 ppm correspond to the CH of biphenyl group (**Ar**), and the signal at 144 ppm to the quaternary carbon between the two phenyl rings (**CAr-CAr**). Evidence of the presence of the triazine ring motif is shown by the ¹³C resonances at 171 ppm assigned to the triazine ring (**CAr=N**).^{3a,23} No signal at around 120 ppm for CN is observed, implying that all the nitrile groups have either reacted to form the triazine ring motif or were otherwise consumed in the reaction. This conclusion would not be possible from the solid-state NMR spectrum acquired without DNP. We also note that overall the resonances are broader than anticipated:³ e.g. two CH signals of the biphenyl ring at 128 and 132 ppm are observed under standard solid-state NMR conditions at 9.4 T (see SI – Fig. S9). This is ascribed to both low temperature and/or paramagnetic broadening, as also observed in MOFs.¹⁸

The boost of sensitivity associated with DNP MAS could be used to further prove the presence of the triazine ring motif by using its ¹⁵N spectra fingerprint without requiring isotopic enrichment.^{4a,24} The ¹H ¹⁵N CP MAS DNP spectrum of **P1** (Fig. 3a) showed a very intense signal at 252 ppm (obtained in less than 1 h), and this was assigned to the nitrogen of the triazine ring (**CAr=N**) based on previous reports.^{4a,24}

The ¹H ¹³C CP MAS spectra of biphenyl triazine-based

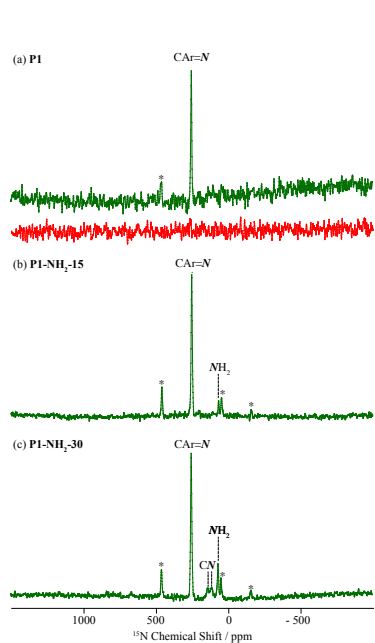


Figure 3. ^1H ^{15}N CP MAS spectrum of (a) **P1**,^{3a} (b) **P1-NH₂-15**, and (c) **P1-NH₂-30** recorded with (green) and without (red) microwave irradiation at $\nu_0(e^-) = 395.2$ GHz, $\nu_0(^1\text{H}) = 600.084$ MHz and $\nu_0(^{15}\text{N}) = 60.83$ MHz. All the acquisition parameters and sample details are identical to Fig. 2. 288 (in (a)), 5120 (in (b)), 4096 (in (c)) scans with a 10 s recycle delay and a 5 ms CP contact time were averaged (experimental time = 48 min in (a), 14 h in (b) and 11 h in (c)).

MOP network **P1-NH₂-15**, prepared with 15 % of an 4-aminocyanobenzene as a monofunctional nitrile was also obtained with microwave irradiation. This also displays an ϵ_{CP} of 13 (Fig. 2b), demonstrating that reproducible enhancement factors could be easily obtained for these materials. Importantly, the presence of the 4-aminobenzene functionality was confirmed in the ^{13}C spectra, with observation of the carbons bearing the NH_2 group (152 ppm, CNH_2) and in the alpha position to it (115 ppm, $\text{C}_{\alpha}(\text{CNH}_2)$). Very interestingly, the ^1H ^{15}N CP MAS DNP spectrum of **P1-NH₂-15** (Fig. 3b) reveals a signal at 66 ppm in addition to the triazine nitrogen ($\text{CAr}=\text{N}$) at 252 ppm, consistent with a neutral primary amine bound to an aromatic carbon (an aniline), and is a remarkable proof of the presence of the 4-aminobenzene functionality. Comparison of this spectrum with the spectrum obtained with a higher concentration of 4-cyanobenzene monomer (**P1-NH₂-30**, Fig. 3c) reveals that the ratio of NH_2 vs. $\text{CAr}=\text{N}$ signal increases from 0.06 to 0.014, and is a further evidence for the incorporation of the functionality into the MOP. Extra resonances at 110 and 136 ppm are also visible and assigned to two different nitrile moieties (seen by IR at 2230 cm^{-1} – see SI).

The fast acquisition of ^1H ^{13}C CP MAS DNP spectra for the MOP materials illustrated in Fig. 2 allowed high throughput NMR spectra (Fig. 4) to be recorded for a large range of polymers **P1-R-X** prepared by combinatorial synthesis (Fig. 1). All of these materials show the characteristic

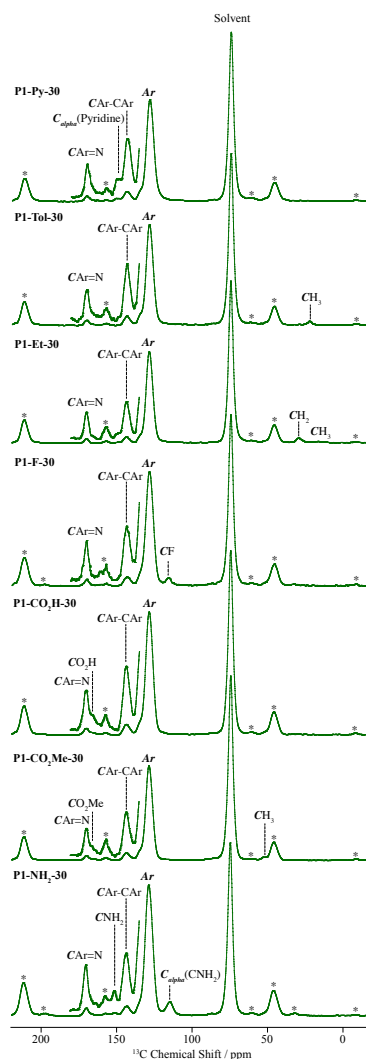


Figure 4. ^1H ^{13}C CP MAS spectrum of biphenyl triazine MOP networks **P1-R-X** (see Fig. 1) recorded with microwave irradiation. All the acquisition parameters and sample details are identical to Fig. 2, except when stated otherwise. 128 or 256 scans were accumulated (see SI). Inserts show a magnified view (x 6) of the 180 - 135 ppm region.

^{13}C (and ^{15}N – see SI) signals of the triazine and biphenyl moieties. More importantly, all ^{13}C spectra present a fingerprint signal of the functionality incorporated into the polymer: e.g., the $\text{C}_{\alpha}(\text{pyridine})$, CH_3 and CO_2H groups of the 4-cyanopyridine, 4-cyanotoluene, 4-cyanobenzoic acid functionalities in **P1-Py-30**, **P1-Tol-30** and **P1-CO₂H-30** are observed at 150, 23 and 167 ppm, respectively.

In conclusion, we have shown that the first chemical application of DNP MAS NMR at 14.1 T allows an enormous boost in speed and efficiency for molecular structure determination in MOPs. In effect, this opens the door for a more detailed characterization of solid-state structure for these materials than is realistic with conventional NMR methods, and may be essential in understanding structure-property relationships for MOP materials in the future.

ASSOCIATED CONTENT

Supporting Information. Details of all synthesis, DNP samples preparation, pore size distribution, IR, BET, comparison of data under DNP and standard NMR conditions. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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